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(71) Applicant (for all designated States except US): BASF CORPORATION [US/US]; Patent Department, 26701 Telegraph Road, Southfield, MI 48034-2442 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): PLASSMANN, William [US/US]; 853 Cherry Lane, Waterville, OH 43566 (US).

(74) Agents: GOLOTA, Mary et al.; BASF Corporation, 26701 Telegraph Road, Southfield, MI 48034-2442 (US).

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(54) Title: COATING COMPOSITIONS HAVING IMPROVED ADHESION TO ALUMINUM SUBSTRATES

(57) Abstract: The invention provides coating compositions having improved adhesion to substrates, especially aluminum substrates. The compositions of the invention are two-component coating compositions having a binder component (I) and a hardener component (II). Binder component (I) has at least one active hydrogen containing compound. Hardener component (II) has an isocyanate functional compound (A), and a silane oligomer (B). Silane oligomer (B) is the reaction product of isocyanate functional compound (A) and a coupling agent (X) comprising (i) at least one alkoxysilane functional group, and (ii) at least one isocyanate reactive group selected from the group consisting of thiol groups secondary amine groups, primary amine groups and mixtures thereof. The silane oligomer (B) comprises at least two free isocyanate groups.

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COATING COMPOSITIONS HAVING IMPROVED ADHESION TO ALUMINUM SUBSTRATES

FIELD OF THE INVENTION

5 The invention relates to two-component coating compositions for use with metallic substrates such as aluminum substrates. More particularly, the invention relates to the use of a particular hardener composition comprising a particular silane oligomer.

BACKGROUND OF THE INVENTION

10 Fuel consumption issues have encouraged automobile manufacturers to explore ways of reducing the total weight per car. One method to achieve automobile weight reduction has been the use of materials other than traditional steel in the production of the various automotive components, including the outer body panels. To this end, plastics, composites, ceramics and lower weight metals have been
15 investigated.

 Lower weight metals, such as aluminum and aluminum alloys, are particularly interesting with respect to the fabrication of outer body panels, wheels and decorative components. Such components are often coated with high performance paint compositions designed to provide both an attractive appearance as well as protection
20 from the environment. However, metals such as aluminum present performance challenges to the coatings formulator which are different than those encountered with traditional steel based systems.

 Aluminum is often pretreated with materials such as chromic acid conversion coatings to facilitate the adherence of subsequently applied coatings. However, such
25 pretreatments are undesirable due to a variety of factors including cost, time, disposal issues and environmental/safety concerns. It is therefore desirable to provide coating compositions which would provide acceptable adhesion to bare, untreated aluminum substrates and still provide desirable appearance and performance properties, especially those required by the automotive industry.

30 Adherence to bare aluminum substrates is an issue for both original equipment manufacturers and autobody repair organizations. Repair procedures often require removal of all existing paint layers. Accordingly, it is also desirable for automotive repair coating compositions to possess superior adhesion to bare, untreated aluminum

substrates and still provide optimum appearance and performance properties. However, unlike coating compositions applied by the automotive assembly plant, automotive repair must cure at either room temperature or at a relatively low temperature, typically below 60° C.

5 Two-component coating compositions are most often used by automotive repair organizations to achieve the necessary balance between low temperature cure and performance properties equivalent to the originally applied finish. A particular problem of prior art two-component compositions has been the obtainment of adequate storage stability with respect to the individual components in combination
10 with the desired adhesion properties for the cured composition resulting from the mixture of the separate components. It is necessary that the separate components of any two-component coating composition be stable and capable of storage for up to twelve (12) months under proper storage conditions.

 Accordingly, it would be advantageous to provide a two-component coating
15 composition which would provide superior adhesion to bare, untreated aluminum substrates and still provide desirable stability, appearance and performance properties, especially as required by the automotive repair industry.

 The prior art has attempted to meet these objectives but continues to seek improvements.

20 For example, U.S. Patent No. 4,625,012 discloses methods for making a moisture curable polyurethane having terminal isocyanate groups and pendant alkoxysilane groups by reacting an isocyanatosilane adduct, having terminal isocyanate groups and at least one hydrolyzable alkoxy group bonded to silicon, with a polyisocyanate and a polyol, as well as sealant compositions containing such a
25 polyurethane.

 U.S. Patent No. 4,374,237 discloses curable isocyanate prepolymers in which all or a portion of the available isocyanate terminal groups have been reacted with a secondary amine-containing silane monomer having two trialkoxy silane groups.

 JP 01149820 A provides a curable composition which contains the reaction
30 product of (i) a particular silyl group- and isocyanate group-containing vinyl polymer; (ii) a polyol; (iii) a polyisocyanate; and, as needed, (iv) an active hydrogen-containing silane coupling agent or isocyanate organosilane.

However, none of these compositions appear to provide the performance and/or application properties indicated above. In particular, none of the prior art compositions provide automotive quality coatings which (i) have superior adhesion to bare aluminum substrates, (ii) have optimum coating appearance and gloss as well as other desirable performance properties, (iii) exhibit desirable cure under typical
5 autobody repair shop conditions, i.e., cure rapidly (i.e., sandable within one (1) to two (2) hours of application) at temperatures of 60°C or less and at humidity levels of 10% or less without sensitivity to ambient cure conditions, and (iv) possess commercially acceptable storage stability.

10 Accordingly, it is an object of this invention to provide coating compositions which provide superior adhesion to bare, untreated aluminum substrates and possess desirable appearance, storage, and performance properties, especially adhesion properties, which meet the requirements of the automotive industry.

It is a further object of the invention to provide such coating compositions
15 which are suitable for use in the repair of OEM automotive finishes.

It is still a further object of the invention to provide a two-component coating composition which has superior adhesion to bare, untreated aluminum substrates and meets the stability, appearance, performance and application requirements of the automotive repair industry.

20 SUMMARY OF THE INVENTION

The foregoing objects have unexpectedly been achieved with the use of the compositions and methods of the instant invention. The invention provides a two-component coating composition and a method of providing a cured coating composition.

25 The two-component coating composition requires a binder component (I) and a hardener component (II). Binder component (I) has at least one active hydrogen containing compound. Hardener component (II) requires an isocyanate functional compound (A) having an average isocyanate functionality of two or more, and a silane oligomer (B). Silane oligomer (B) is the reaction product of isocyanate (A) and a
30 coupling agent (X). Coupling agent (X) must have (i) at least one alkoxysilane functional group, and (ii) at least one group reactive with isocyanate selected from the group consisting of thiol groups, secondary amine groups, primary amine groups and

mixtures thereof. The silane oligomer (B) comprises at least two free isocyanate groups.

The method of the invention requires the provision of the two-component coating composition of the invention, ~~mixing the binder component (I) with the~~
5 ~~hardener component (II)~~ to provide a curable coating composition, applying the curable coating composition to a substrate to provide a curable coated substrate, and subjecting the curable coated substrate to conditions sufficient to effect cure and provide a cured coated substrate.

DETAILED DESCRIPTION OF THE INVENTION

10 The curable coating composition of the invention is a two-component coating composition. As used herein, the term "two-component" refers to the number of solutions and/or dispersions which are mixed together to provide a curable coating composition. Up until the point of mixing, neither of the individual components alone provides a curable coating composition.

15 Once mixed, the resulting curable coating composition is applied to a substrate as quickly as possible. Typically, "as quickly as possible" means immediately after the mixing of the separate components or within eight (8) hours from the time the separate components are mixed, preferably less than one (1) hour after mixing. In a typical two-component application process the components are mixed together either
20 (i) at the nozzle of a sprayer by the joining of two separate carrier lines at the nozzle or (ii) immediately upstream of the nozzle of a sprayer and then delivered to the nozzle via a single carrier line. Once at the nozzle, the mixture is immediately atomized into a mist which is directed at a substrate which is being coated with a film of the mixture of the two-components.

25 Unlike one-component compositions, two-component compositions will generally cure in the absence of elevated temperatures. The individual components (I) and (II) will react with each other upon admixture to provide a crosslinked product, most often at ambient temperatures, or more particularly at temperatures of from 15 to 60° C and most preferably from 24 to 60°C.

30 The two-component coating composition comprises a binder component (I) and a hardener component (II).

The binder component (I) must have at least one active hydrogen-containing compound. The at least one hydrogen containing compound will generally be a

polymer having at least one group reactive with isocyanate functionality. Groups reactive with isocyanate functionality include, for example, hydroxyl groups, amino groups, thiol groups, hydrazine groups, and mixtures thereof. Illustrative polymers containing such functional groups include, for example, acrylic polymers, modified acrylic polymers, polyesters, polyepoxides, polycarbonates, polyurethanes, polyamides, polyimides, and mixtures thereof.

In one preferred embodiment of the invention, the polymer is an acrylic. Such polymers are well-known in the art, and can be prepared from monomers such as methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, and the like. Nonfunctional monomers such as acrylate esters and styrene can also be incorporated. The functional group that is reactive with isocyanate, e.g., hydroxyl, can be incorporated into the ester portion of the acrylic monomer. For example, hydroxy-functional acrylic monomers that can be used to form such polymers include hydroxyethyl acrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, hydroxypropyl acrylate, and the like. Aminofunctional acrylic monomers would include t-butylaminoethyl methacrylate and t-butylaminoethylacrylate. Other acrylic monomers having isocyanate-reactive functional groups in the ester portion of the monomer are also within the skill of the art.

In a particularly preferred embodiment, the binder (I) will comprise at least one acrylic polymer prepared from monomers selected from the group consisting of acrylic acid, methacrylic acid, acrylate alkyl esters, hydroxyfunctional acrylate esters, ethylencially unsaturated nonfunctional monomers and mixtures thereof. Such a polymer will generally have an number average molecular weight in the range of from 1000 to 50,000, a hydroxyl number of from 200 to 3000 mg KOH/g, and an acid number in the range of from 0.1 to 25 mg KOH/g.

Modified acrylics can also be used as the at least one active hydrogen containing comopound according to the invention. Such acrylics are typically polyester-modified acrylics or polyurethane-modified acrylics, as is well known in the art. An example of one preferred polyester-modified acrylic is an acrylic polymer modified with δ -caprolactone. Such a polyester-modified acrylic is described in U.S. Pat. No. 4,546,046 of Etzell et al, the disclosure of which is incorporated herein by reference. Polyurethane-modified acrylics are also well known in the art. They are

described, for example, in U.S. Pat. No. 4,584,354, the disclosure of which is incorporated herein by reference.

5 Polyesters having hydroxyl groups, acid groups, or amino groups as isocyanate-reactive groups can also be used as in component (I) in the composition according to the invention. Such polyesters are well-known in the art, and may be prepared by the polyesterification of organic polycarboxylic acids (e.g., phthalic acid, hexahydrophthalic acid, adipic acid, maleic acid) or their anhydrides with organic polyols containing primary or secondary hydroxyl groups (e.g., ethylene glycol, butylene glycol, neopentyl glycol).

10 Other polymers suitable for use in binder (I) include polyurethanes and polyureas. Polyurethanes having active hydrogen functional groups are also well-known in the art. They are prepared by a chain extension reaction of a polyisocyanate (e.g., hexamethylene diisocyanate, isophorone diisocyanate, MDI, etc.) and a polyol (e.g., 1,6-hexanediol, 1,4-butanediol, neopentyl glycol, trimethylol propane).

15 Similarly, polyureas having active hydrogen functional groups are prepared by the reaction of a isocyanate functional compound, such as is discussed above for the preparation of polyurethanes, with amines such as primary and secondary amines. Both polyurethanes and polyureas can be provided with active hydrogen functional groups by capping the polymer chain with an excess of diol, polyamine, amino
20 alcohol, or the like.

Binder component (I) may also comprise further agents and/or additives which impart a desired characteristic to the coating composition, the process, or to the cured coating made therefrom. Illustrative examples include diluents, solvents, pigments, fillers, extenders, dyes, surfactants, stabilizers, wetting agents, dispersing agents,
25 rheology control agents, leveling agents, catalysts, cure inhibiting agents, anti-yellowing agents, free radical scavengers, melamine, and anti-cratering agents, mixtures thereof, and the like.

Examples of preferred diluents include low molecular weight polyols such as
those described in U.S. Patent No. 4,314,918, aspartatic adducts such as those
30 described in US Patent Nos. 5,214,086, 5,661,216, and the like.

Component (I) will generally comprise from 10 to 100 percent by weight nonvolatile of the at least one active hydrogen containing compound, and preferably from 20 to 60 weight percent nonvolatile and most preferably from 25 to 50 percent

by weight nonvolatile, based on the total weight of component (I).

The two-component composition of the invention further requires a hardener composition (II). The hardener component (II) must comprise an isocyanate functional compound (A) and a silane oligomer (B).

5 Suitable isocyanate functional compounds (A) include polyisocyanates which are aliphatic, including cycloaliphatic polyisocyanates, or aromatic. Useful aliphatic polyisocyanates include aliphatic diisocyanates such as ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, 1,4-butylene diisocyanate, lysine diisocyanate, hexamethylene diisocyanate (HDI), 1,4-methylene
10 bis-(cyclohexylisocyanate) and isophorone diisocyanate. Useful aromatic diisocyanates include the various isomers of toluene diisocyanate, meta-xylenediisocyanate and para-xylenediisocyanate, also 4-chloro-1,3-phenylene diisocyanate, 1,5-tetrahydro-naphthalene diisocyanate, 4,4'-dibenzyl diisocyanate and 1,2,4-benzene triisocyanate can be used. In addition, the various isomers of
15 .alpha.,.alpha.,.alpha.,.alpha.'-tetramethyl xylene diisocyanate can be used. Aliphatic polyisocyanates are preferred, particularly hexamethylene diisocyanate and isophorone diisocyanate.

Also suitable for use are the biurets, aliphonates and/or isocyanurates of such aliphatic or aromatic polyisocyanates. Preferred for use as isocyanate functional
20 compounds (A) are the biurets and isocyanurate of polyisocyanates, especially of the aliphatic polyisocyanates such as hexamethylene diisocyanate and isophorone diisocyanate. Most preferred for use as the isocyanate functional compounds (A) are the biurets and isocyanurates of hexamethylene diisocyanate.

25 Suitable isocyanate functional compounds (A) will have an average isocyanate functionality of at from 2 to 5, preferably at least two and more preferably from 3 to 4. Ideally, isocyanate functional compound (A) will generally have at least two free or reactable isocyanate groups per molecule and more preferably will have three free functional groups per molecule. However, it will be appreciated that commercially available isocyanate functional compounds will generally not be pure compounds. As
30 a result, a commercially available isocyanate functional compound intended to have three free isocyanate groups per molecule will have an average isocyanate functionality of greater than 3, generally from 3 to 4.

In addition to isocyanate functional compound (A), hardener (II) will also comprise a silane oligomer (B) which is the reaction product of compound (A) and a coupling agent (X). Silane oligomers (B) suitable for use in the instant invention will have at least two free isocyanate groups.

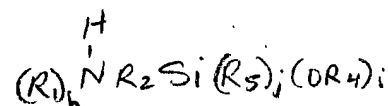
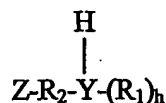
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Silane oligomer (B) results from the reaction of an isocyanate functional compound (A) and a coupling agent (X).

The reaction between coupling agent (X) and an isocyanate functional compound (A) will occur at ambient temperatures of from 10 to 30 °C. It will be appreciated that isocyanate functional compound (A) reacted with coupling agent (X) may be the same or different as the isocyanate functional compound (A) used in hardener component (II) of the coating composition of the invention. In a most preferred embodiment, the compound (A) reacted with coupling agent (X) will be the same as the compound (A) present in the hardener component (II) of the coating composition of the invention.

The reactants (X) and (A) may be reacted in situ in a hardener component (II) or in a separate reaction area. In the latter case, the resulting oligomer (B) will be subsequently added to an intended hardener component (II). In a preferred embodiment of the invention, the coupling agent (X) will be added directly to a hardener component (II). In this embodiment, the resulting silane oligomer (B) is produced via the in situ reaction at ambient temperature of isocyanate functional compound (A) and coupling agent (X) in hardener component (II). In a most preferred embodiment, the isocyanate functional compound (A) reacted in situ in the component (II) with coupling agent (X) is the same as the isocyanate functional compound (A) in component (II).

Coupling agent (X) must have (i) at least one alkoxy silane functional group, and (ii) at least one group reactive with isocyanate selected from the group consisting of thiol groups, secondary amine groups, primary amine groups and mixtures thereof. Preferred coupling agents (X) are aminosilanes, and most preferably, coupling agent (X) will be an aminosilane having at least one secondary amino group. In a particularly preferred embodiment of the invention, coupling agent (X) will have the formula:



5 wherein the variables Z, R₁, R₂, Y and h are defined as follows.

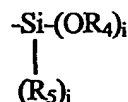
R₁ may be selected from the group consisting of hydrogen, alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, groups of the formula R₂-Z wherein Z and R₂ are as defined below, and mixtures thereof. Preferably, R₁ will be R₂-Z as defined below.

10 h is a number from 0 to 1, but is most preferably 1, especially when Y is N. Y may be N or S but with the proviso that when Y is S, h = 0. Y is most preferably N.

R₂ is selected from the group consisting of alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, heteroatomic groups containing atoms selected from the group consisting of Si, O, and mixtures thereof, and mixtures thereof. Preferably,
 15 R₂ will be an alkyl group, cycloaliphatic group, aromatic group, or arylalkyl group of from 1 to 18 carbons, with alkyl groups and cycloaliphatic groups being more preferred, especially alkyl groups of from 1 to 5. R₁ and R₂ need not be identical, although they may be if so desired.

Z is a siloxy-containing group of the formula:

20



25 where R₄ and R₅ may be selected from the group consisting of alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, and mixtures thereof. Preferably, R₄ and R₅ will be an alkyl group, cycloaliphatic group, aromatic group, or arylalkyl group of from 1 to 18 carbons, with alkyl groups and cycloaliphatic groups being more preferred, especially alkyl groups of from 1 to 5. R₄ and R₅ need not be
 30 identical, although they may be if so desired.

i is a number from 1 to 3, preferably 2 or 3 and most preferably 3, while j is a number equal to 3 - i.

An example of a most preferred coupling agent (X) is ~~bis-(gamma-trimethoxysilylpropyl)amine~~ commercially available from Witco Chemical as A-1170
 35 aminosilane.

Generally, from 0.1 to 20.0 weight percent of (X) may be added to component (II), based on the nonvolatile weight of compound (A), preferably from 0.5 to 15.0 weight percent, based on the nonvolatile weight of (A), and most preferably from 1.0 to 10.0 weight percent, based on the nonvolatile weight of (A). Coupling agent (X) and compound (A) will generally be reacted in no more than a 1:1 stoichiometric ratio, preferably less than a 1:1 stoichiometric ratio, and most preferably from 0.2:1 to 0.01:1.

It has been unexpectedly been found that the structure of (X) influences the allowed concentration of silane oligomer (B) and isocyanate functional compound (A) in hardener component (II). For example, when R_1 of coupling agent (X) is hydrogen, hardener component (II) of the invention must have a weight percent nonvolatile of no more than 25.0 weight percent nonvolatile, preferably from 5.0 to 20.0 weight percent nonvolatile, most preferably from 5.0 to 10.0 weight percent nonvolatile, based on the total weight of hardener component (II). However, when R_1 is not hydrogen, the hardener component (II) of the invention may have a weight percent nonvolatile of from 5.0 to 100.0 weight percent, preferably from 10 to 90 weight percent nonvolatile, and most preferably from 20 to 80 weight percent nonvolatile, based on the total weight of hardener component (II).

Thus, when R_1 is hydrogen, there will generally be from 0.1 to 20.0 weight percent of silane oligomer (B), based on the nonvolatile weight of hardener component (II) of the invention, and preferably from 0.5 to 15.0 weight percent of silane oligomer (B), based on the nonvolatile weight of hardener component (II), and most preferably from 1.0 to 10.0 weight percent of the silane oligomer (B), based on the nonvolatile weight of hardener component (II). When R_1 is not hydrogen, there will generally be from 0.1 to 20.0 weight percent of silane oligomer (B), based on the nonvolatile weight of hardener component (II) of the invention, and preferably from 0.5 to 15.0 weight percent of silane oligomer (B), based on the nonvolatile weight of hardener component (II), and most preferably from 1.0 to 10.0 weight percent of the silane oligomer (B), based on the nonvolatile weight of hardener component (II).

Component (II) may also comprise further agents and/or additives which impart a desired characteristic to the coating composition, the process, or to the cured coating made therefrom. Illustrative examples include diluents, solvents, pigments, fillers, extenders, dyes, surfactants, stabilizers, wetting agents, dispersing agents,

rheology control agents, leveling agents, catalysts, cure inhibiting agents, anti-yellowing agents, free radical scavengers, melamine, and anti-cratering agents, mixtures thereof, and the like. However, in the preferred embodiments of the invention, such agents and/or additives will be preferably in the component (I) other than one or more catalysts which will preferably be present in component (II).
5 Examples of suitable catalysts for use in component (II) include tertiary amines, dibutyltindilaurate, zinc octoate and the like.

Component (II) may also comprise one or more solvents. In a preferred embodiment, component (II) will include one or more solvents. Suitable solvents and/or diluents include aromatics, naphthas, acetates, ethers, esters, ketones, ether esters and mixtures thereof.
10

The composition of the present invention may further comprise any additional ingredient which imparts any desired characteristic to the composition, or to the process, or to the curable or cured coating composition made therefrom. Such additional ingredients comprise rheology control agents, leveling agents, catalysts, cure inhibiting agents, anti-yellowing agents, free radical scavengers, melamine, and anti-cratering agents. Such additives may be present in component (I) or component (II) but as indicated above, will preferably be present in component (I).
15

In the process of the present invention, the two-component composition of the invention is provided and mixed to provide a curable coating composition. The resulting curable coating composition is then applied to a substrate to provide a film or a coated substrate, following which the coated substrate is cured to provide a cured coated substrate.
20

The step of applying the curable coating composition to a substrate will typically occur within 8 hours of mixing the components (I) and (II), preferably within 4 hours of mixing, more preferably within 1 hour, and most preferably within 30 minutes of mixing components (I) and (II).
25

The process of the invention may be used with any substrate onto which a coating formulation can be applied and cured. Preferably, the substrate will be metallic, polymeric, amorphous (e.g. glass), or a mixture thereof. Most preferably, the substrate is an aluminum substrate and most especially a bare, untreated aluminum substrate suitable for use as an automotive body panel or component.
30

In the process of the present invention, the two-component composition to be

used is the composition of the present invention, as has been described in detail above. A preferred process of the present invention utilizes the preferred composition of the present invention, as has also been described in detail above. A most preferred process of the present invention utilizes a most preferred composition of the present invention,
5 as has also been described in detail above.

In general, the two-component composition of the present invention may be opaque or transparent, colored or colorless. The coating composition may thus be utilized in a process whereby it is a first coating on the substrate, an intermediate coating on the substrate, or an uppermost coating on the substrate. However, it is
10 preferred that the coating composition is both pigmented and most preferably pigmented to provide corrosion protection for the underlying metallic substrate. It is also preferred that the coating composition is utilized in a process whereby it forms the lowermost coating on the substrate, i.e. it is applied directly to the bare untreated metal, preferably aluminum substrate. Thus it is preferred that the coating composition
15 of the present invention is used to form an automotive quality primer for use over bare, untreated aluminum.

Although the following Examples illustrate different embodiments of the present invention, the present invention is not limited to or by these examples.

EXAMPLE 1

20 Two-Component Clearcoat according to the Invention.

A two-component clearcoat according to the invention was prepared as follows. A hardener component was prepared by mixing 28.4 parts of A-1170, an amino silane commercially available from Witco Chemical, with 400.0 parts of a commercially available HDI based hardener from BASF Corporation of Whitehouse,
25 OH.¹ The hardener component of the invention was then mixed 1:4 (volume) with a commercially available acrylic based clearcoat composition from BASF Corporation.²

EXAMPLE 2

Comparison of the Two-Component Clearcoat of the Invention.

The clearcoat of Example 1 was compared with a control two-component
30 clearcoat. The control clearcoat was prepared by mixing 4 volume parts of BASF's DC88 Clear with 1 volume part of BASF's DH45 Hardener. Both clearcoats were

¹ BASF's DH45 Hardener.

² BASF's DC88 Clear.

sprayed applied to aluminum panels (Q-Panel, Aluminum, Mill Finish 3105 H24). The aluminum panels were prepared with a solvent wash commercially available from BASF Corporation as BASF #900 solvent wash. Both panels had approximately 2.0 mils dried film after curing for seven days at 73 degrees F. Initial adhesion loss for the control clearcoat was 100% while the initial adhesion loss for the clearcoat of the invention was 4%. Adhesion loss was measured with the cross hatch adhesion test, i.e., a 1" x 1" block of 25 squares was cut using a grid, with each square representing 4% of the total measured adhesion. The panels were then placed in a 100% Relative Humidity test at 100 degrees F for 96 hours. Final adhesion for the control clearcoat was 100%, while the clearcoat of the invention had 0% final adhesion loss.

EXAMPLE 3

Two-Component Primer according to the Invention.

A two-component primer according to the invention was prepared as follows. A hardener component was prepared by mixing 0.38 parts of A-1170, an amino silane commercially available from Witco Chemical, with 6.17 parts of a commercially available HDI based hardener from BASF Corporation and 17.11 parts of a commercially available reducer from BASF.³ The resulting hardener component of the invention was then mixed 2:4 (volume) with a commercially available acrylic based primer composition from BASF Corporation.⁴

EXAMPLE 4

Comparison of the Two-Component Primer of the Invention.

A control two-component primer was prepared by mixing 4 volume parts of BASF's DP20 Primer with 2 volume parts of BASF's commercially available DH46 Hardener/PR80 Reducer blend.

Both primers were sprayed applied to aluminum panels (Q-Panel, Aluminum, Mill Finish 3105 H24). The aluminum panels were prepared with a solvent wash commercially available from BASF Corporation as BASF #900 solvent wash. Both panels had approximately 2.0 mils primer which was sanded with P400 grit sandpaper approximately 120 minutes after spray application. A basecoat layer of R-M® Diamont "Blue OEM" mixed 4:3:0.4 by volume with PR80 Reducer and BASF's DH46 Hardener was then spray applied. The basecoat was flashed for 15 minutes at

³ BASF's DH46 Hardener and PR80 Reducer.

⁴ BASF's DP20 Primer.

ambient followed by spray application of a clearcoat layer of BASF's commercially available DC92 Clear mixed 3:1:1 by volume with DH46 Hardener and PR80 Reducer. All panels had approximately 1.0 mils of basecoat and 2.0 mils of clearcoat. The prepared panels were then cured for 7 days at 73 degrees F.

- 5 Initial adhesion loss for the control panel was 4% while the initial adhesion loss for the panel containing the primer of the invention was 0%. Adhesion loss was measured as in Example 2.

- The panels were then placed in a 100% Relative Humidity test at 100 degrees F for 192 hours. Final adhesion loss for the control panel was 100%, while the panel
10 containing the primer composition of the invention had 0% final adhesion loss.

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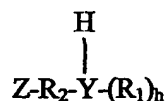
CLAIMS

I claim:

1. A two-component coating composition comprising
a binder component (I) comprising at least one active hydrogen containing
5 compound, and
a hardener component (II) comprising
 - (A) an isocyanate functional compound, and
 - (B) a silane oligomer comprising the reaction product of (A) and a
coupling agent (X) comprising
 - 10 (i) at least one alkoxy silane functional group, and
 - (ii) at least one group reactive with isocyanate selected
from the group consisting of thiol groups, secondary
amine groups, primary amine groups and mixtures
thereof,
- 15 wherein the silane oligomer (B) comprises an average of at least two free isocyanate
groups.

2. The two-component coating composition of claim 1, further comprising the
coupling agent (X) having the formula:

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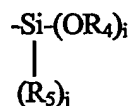
where

- 25 R_1 is selected from the group consisting of hydrogen, alkyl groups,
cycloaliphatic groups, aromatic groups, arylalkyl groups, groups of the formula $\text{R}_2\text{-Z}$
wherein Z and R_2 are as defined below, and mixtures thereof,

 h is a number from 0 to 1, Y may be N or S but with the proviso that when Y is S, $h = 0$,

- 30 R_2 is selected from the group consisting of alkyl groups, cycloaliphatic groups,
aromatic groups, arylalkyl groups, heteratomic groups containing atoms selected from
the group consisting of Si, O, and mixtures thereof, and mixtures thereof, and

 Z is a siloxy-containing group of the formula:



5

where R_4 and R_5 may or may not be the same and are selected from the group consisting of alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, and mixtures thereof, i is 1, 2 or 3, and j is equal to $3 - i$.

10 3. The two-component coating composition of claim 2 wherein coupling agent (X) is bis-(gamma-trimethoxysilylpropyl)amine.

4. The two-component coating composition of claim 1 wherein compound (A) has an average isocyanate functionality of between 2 and 3.

15

5. The two-component coating composition of claim 4 wherein compound (A) is selected from the group consisting of hexamethylene diisocyanate isocyanurate, the biuret of hexamethylene diisocyanate, the oligophantate of hexamethylene diisocyanate, isophorone diisocyanate isocyanurate, the biuret of isophorone diisocyanate, the
20 oligophantate of isophorone diisocyanate and mixtures thereof.

6. The two-component coating composition of claim 1 wherein silane oligomer (B) is present in the hardener component (II) in an amount of from 0.1 to 20.0 % by weight, based on the total nonvolatile weight of the hardener component (II).

25

7. The two-component coating composition of claim 1 wherein silane oligomer (B) is the reaction product of from 0.1 to 80.0 weight percent of coupling agent (X) added to an isocyanate functional compound (A), based on the nonvolatile weight of (A).

30

8. A process of providing a cured coating composition, comprising providing a two-component coating composition comprising a binder component (I) comprising at least one active hydrogen containing compound, and

a hardener component (II) comprising

- (A) an isocyanate functional compound, and
- (Bi) a silane oligomer comprising the reaction product of

(A) and a coupling agent (X) comprising

- (i) at least one alkoxysilane functional group, and
- (ii) at least one group reactive with isocyanate selected from the group consisting of thiol groups, secondary amine groups, primary amine groups and mixtures thereof,

wherein the silane oligomer (B) comprises at least two free isocyanate groups,

mixing the binder component (I) with the hardener component (II) to provide a curable coating composition,

applying the curable coating composition to a substrate to provide a curable coated substrate, and

subjecting the curable coated substrate to conditions sufficient to effect cure and provide a cured coated substrate.

9. The process of claim 8, wherein the coupling agent (X) is of the formula:



where

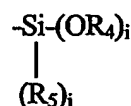
R₁ is selected from the group consisting of hydrogen, alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, groups of the formula R₂-Z wherein Z and R₂ are as defined below, and mixtures thereof,

h is a number from 0 to 1,

Y may be N or S but with the proviso that when Y is S, h = 0,

R₂ is selected from the group consisting of alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, heteratomic groups containing atoms selected from the group consisting of Si, O, and mixtures thereof, and mixtures thereof, and

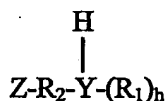
Z is a siloxy-containing group of the formula:



5

where R_4 and R_5 may or may not be the same and are selected from the group consisting of alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, and mixtures thereof, i is 1, 2 or 3, and j is equal to $3 - i$.

- 10 10. A two-component coating composition comprising
a binder component (I) comprising at least one active hydrogen containing
compound, and
a hardener component (II) consisting essentially of
- (A) an isocyanate functional compound having an average
15 isocyanate functionality of between 2.5 and 4.0, and
(B) a silane oligomer comprising the reaction product of (A) and a
coupling agent (X) of the formula:



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where

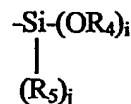
R_1 is selected from the group consisting of hydrogen, alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, groups of the formula $R_2\text{-Z}$ wherein Z and R_2 are as defined below, and mixtures thereof,

25 h is a number from 0 to 1,

Y may be N or S but with the proviso that when Y is S, $h = 0$,

R_2 is selected from the group consisting of alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, heteratomic groups containing atoms selected from the group consisting of Si, O, and mixtures thereof, and mixtures thereof, and

30 Z is a siloxy-containing group of the formula:



35

where R_4 and R_5 may or may not be the same and are selected from the group consisting of alkyl groups, cycloaliphatic groups, aromatic groups, arylalkyl groups, and mixtures thereof, i is 1, 2 or 3, and j is equal to $3 - i$.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/15017

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/80 C09D175/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 108, no. 22, May 1988 (1988-05) Columbus, Ohio, US; abstract no. 188507w, "Urethane prepolymers as curing agents for coatings" page 88; column 1; XP002183616 abstract & JP 62 250021 A (NATOCO PAINT) 30 October 1987 (1987-10-30)	1-5,7-10
X	EP 0 096 250 A (DYNAMIT NOBEL) 21 December 1983 (1983-12-21) page 4, line 23 -page 8, line 20; claims 1-5; examples -/-	1-10

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

21 November 2001

Date of mailing of the international search report

06/12/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bourgonje, A

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 01/15017

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 480 089 A (DAINICHISEIKA COLOR&CHEMICALS) 15 April 1992 (1992-04-15) page 8, line 41 -page 9, line 53 page 30, line 44 - line 51; claim 1	1
X	EP 0 994 117 A (BAYER) 19 April 2000 (2000-04-19) page 2, line 43 -page 3, line 15; claim 1	1
X	US 5 238 993 A (HSIEH) 24 August 1993 (1993-08-24) column 2, line 28 -column 4, line 10	1,3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/15017

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 62250021	A	30-10-1987	JP 2060347 C JP 7084574 B	10-06-1996 13-09-1995
EP 96250	A	21-12-1983	DE 3220866 A1 AT 25460 T DE 3369786 D1 EP 0096250 A1 ES 522895 D0 ES 8403513 A1 JP 1703318 C JP 3070733 B JP 58219211 A US 4474933 A	08-12-1983 15-02-1987 19-03-1987 21-12-1983 16-03-1984 16-06-1984 14-10-1992 08-11-1991 20-12-1983 02-10-1984
EP 480089	A	15-04-1992	US 5321083 A EP 0480089 A1 DE 69027432 D1 DE 69027432 T2	14-06-1994 15-04-1992 18-07-1996 23-01-1997
EP 994117	A	19-04-2000	US 6046270 A EP 0994117 A1 JP 2000119365 A	04-04-2000 19-04-2000 25-04-2000
US 5238993	A	24-08-1993	AU 669749 B2 AU 5103093 A BR 9307218 A CN 1087659 A ,B JP 8501820 T MX 9306137 A1 WO 9407933 A1 ZA 9307304 A	20-06-1996 26-04-1994 25-05-1999 08-06-1994 27-02-1996 30-06-1994 14-04-1994 03-04-1995